Antioxidants from Tar Acids

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Before delving into the subject at hand, namely the manufacture of antioxidants from tar acids, it would be wise for us to define our terms and the scope of this discussion. By tar acids we mean the "acidic" or base-soluble fraction of coal tar. These same tar acids are also available from petroleum sources. Furthermore, both phenol, parent compound of the tar acids, and p-cresol are made synthetically. While phenol is the major constituent of tar acids, the synthetic material accounts for over 90% of the market. Its precursors, benzene or toluene, are also coal chemicals which are again mostly derived from petroleum sources. Benzene is also the starting material for styrene, an important chemical intermediate in the antioxidant field. As far as the end products are concerned, we shall limit our discussion to the phenolic antioxidants, realizing at the same time that there are non-phenolic antioxidants prepared from tar acids as there are phenolic antioxidants not prepared from tar acids. It is apparent that the coal tar industry does not enjoy an exclusive position as supplier of raw materials for the manufacture of phenolic antioxidants.

Despite the fact that the coal tar industry was at one time the only producer of tar acids, the early work on phenolic antioxidants was not done by this industry. Rather, those industries manufacturing items subject to oxidative degradation saw a need to stabilize their products and therefore investigated the use of antioxidants. Such industries include gasoline, food and animal feed, rubber and plastics, lubricating and transformer oils. As a result, most of the research, both that dealing with the theoretical aspects of oxidation and inhibition, and that dealing with the development of new and better antioxidants, was carried out by the potential users of antioxidants. Even the manufacture of antioxidants has been almost exclusively in the hands of the users and a few chemical manufacturers.

The application of phenolic antioxidants in the various fields was based on the finding by Moureu and his co-workers (1) that acrolein could be stabilized by the addition of certain phenols in small amounts. The use of stabilizers such as tannin and hydroquinone in rubber was described by Helbronner and Bernstein (2). At the 71st meeting of the Americal Chemical Society at Tulsa, in April of 1926, Smith and Wood (3) presented a paper entitled "Inhibiting Agents in the Oxidation of Unsaturated Organic Compounds" dealing with the oxidation inhibition in soaps, fats and oils. In the gasoline field, an initial emphasis on color stabilization gave way to gum prevention by inhibitors (4,5).

Closer scrutiny of the type of substances used in these and other applications led to theories on the mechanism of the oxidative degradation, its inhibition, and subsequently, to a more systematic study of the types of compounds which may be used advantageously to perform this function.

Here are several recent references which may serve as a starting point for those who wish to pursue this phase further.

Lundberg(6) recently edited a monograph entitled "Antioxidation and Antioxidants." Ingold (7) also reviewed the literature in 1961. A recent paper presented before the Division of Petroleum Chemistry at the last ACS meeting at Atlantic City was that by Hedenburg (8) of the Gulf Research Laboratories.

In the studies performed to find a correlation between the structure of an antioxidant and its activity, whole groups of substituted phenols were prepared and tested (9-15) as antioxidants. This led to the finding that sterically hindered phenols, i.e. phenols in which the hydroxyl group is sterically hindered, gave the desired properties. In general, it was found that the more hindered the phenol was, the better was its antioxidant activity. However, only last year it was found by Spacht and his co-workers at Goodyear(16) that too much steric hindrance had a deleterious effect on antioxidant activity.

Let us consider the commercial phenolic antioxidants and the modes of their manufacture. Of primary interest is 2,6-di-t-butyl-p-cresol (I). Some 17 million pounds of this compound was produced in 1961. Even at that, it may not be the phenolic antioxidant made in greatest quantity, but it has been used most widely including all the applications mentioned earlier. It is known in the food industry as BHT (which stands for butylated hydroxy toluene) and the various manufacturers have their own trade name for it.

When we look at the structure we immediately realize that it is the reaction product of p-cresol and a source of t-butyl groups, such as isobutylene, t-butyl chloride or t-butyl alcohol. Of these, the olefin is preferred for ease of operation and for reasons of economics. While synthetic p-cresol is available and is the source of most of the BHT produced, those active in the coal tar field will have realized immediately another source of p-cresol, namely the tar acids. There is one difficulty, however - p-cresol occurs along with its more abundant isomer, m-cresol, from which it cannot be separated by fractional distillation; the two isomers boil within one degree of each other. Various physical means of separation have been investigated but it turns out that conversion to the desired compound, BHT, is one of the simplest means of separating meta- and para-cresol (17,18,19). This is made possible again by a phenomenon which was mentioned before, namely steric hindrance. When a mixture of meta- and para-cresol is alkylated with isobutylene, the initial products are mono t-butyl derivatives. In the case of p-cresol (II), the t-butyl group enters the position ortho to the hydroxyl group as expected by the stronger ortho-para directing influence of the hydroxyl group over that of the methyl group. Since both ortho-positions are identical, only one compound will be formed. This compound is 2-t-butyl-p-cresol (III). In the case of m-cresol (IV), there are three choices, two dissimilar ortho positions as well as an open para position. However, steric hindrance prevents the introduction of the t-butyl group in the ortho position between the hydroxyl and the methyl groups. As a matter of fact, steric hindrance between a methyl and an adjacent t-butyl group makes the normally more stable position para to the hydroxyl group thermodynamically less stable so that the t-butyl group positions itself ortho to the hydroxyl and para to the methyl group to give us 6-t-butyl-m-cresol (V). Unfortunately, the compound described in the literature for many years (18,20,21,22) as 4-t-butyl-m-cresol was actually 6-t-butyl-m-cresol (23-26). The real 4-t-butyl-m-cresol was not made until about 1948 (27,28,29). The two ortho-t-butylated cresols which are thus obtained as the first reaction products from the treatment of m,p-cresol with isobutylene, are also inseparable by fractional distillation.

Further alkylation produces the dibutyl derivatives; on the one hand, the desired compound, 2,6-di-t-butyl-p-cresol, and, as the m-cresol derivative, the para alkylated 4,6-di-t-butyl-m-cresol (VI). These two compounds, the first, an ortho-ortho dibutylated cresol and the latter, an ortho-para dibutylated cresol have boiling points sufficiently far apart for easy separation by fractional distillation. The

distilled BHT can be further purified by washing and crystallization. When p-cresol is made synthetically, it is not admixed with its meta isomer. The alkylation of pure p-cresol is the same as that described for the mixed isomers.

No mention was made of any conditions for the alkylation nor was the catalyst identified. The reason for these apparent omissions is that a variety of alkylation catalysts, such as sulfuric acid, sulfonic acids, phosphoric acid, boron fluoride and solid catalysts, is possible even if we restrict ourselves to isobutylene as the alkylating agent. Furthermore, each catalyst may be used in various concentrations. These factors permit great latitude in the choice of the other reaction conditions such as time and temperature.

A second antioxidant, which has been known for its activity, but which is not widely used in the U.S., is 6-t-butyl-2,4-xylenol (VII). I specified the American market, because it is a commercial product of long standing in Great Britain.

Looking at its structure, one will immediately realize its close structural relationship to BHT. The difference between the two compounds is the replacement of one of the o-t-butyl groups in BHT by a methyl group.

As in the case with m,p-cresol, one of the precursors for 6-t-butyl-2,4-xylenol, namely 2,4-xylenol (VIII), occurs, in tar acid along with its isomer, 2,5-xylenol (IX). The ratio of the two is roughly 2:1 in favor of the 2,4-isomer. While other xylenols are separable from the desired isomer by distillation, the above two isomers boil within one degree of each other.

Again, one can resort to t-butylation not only as a means of obtaining our desired antioxidant but also as a means of separating the two xylenol isomers. The same principles which have been discussed in the m,p-cresol alkylation apply in the present case. As a matter of fact, the mixture of 2,4- and 2,5-xylenol may be viewed as a mixture of ortho-alkylated m,p-cresols, the 2,4-xylenol being the ortho-substituted p-cresol, and the 2,5-xylenol, the ortho-substituted m-cresol. This makes them comparable to the mono-butyl m,p-cresol, each of which can only be t-butylated further with one group. In the one case, the second group entered the free ortho position to give BHT, and in the second, the para position. In the xylenols, one also finds that 2,4-xylenol t-alkylates in the accessible 6-position to give the desired compound, 6-t-butyl-2,4-xylenol while in the case of 2,5-xylenol, the 4- position is alkylated to give 4-t-butyl-2,5-xylenol (X) (19).

The isolation of the desired compound may be accomplished in various ways. One means, which is also applicable to the di-t-alkylation of m,p-cresol, takes advantage of the difference in the reactivity of the two isomers. Therefore, by using a limited amount of the olefin, choosing reaction conditions mild enough to enhance the selectivity, and limiting the reaction time to suppress or at least reduce equilibration, it is possible to alkylate 2,4-xylenol in preference to the 2,5-isomer (30).

The unreacted xylenols, now predominantly the 2,5-isomer, are removed by distillation from the 6-t-butyl-2,5-xylenol.

Another method of isolating 6-t-butyl-2,4-xylenol made from 2,4-2,5-xylenol is to carry the reaction further than in the previous example so that 4-t-butyl-2,5-xylenol is formed in appreciable amounts. The reaction mixture is then added to dilute caustic which dissolves only the non-hindered phenols, namely any unreacted xylenols and the 4-t-butyl-2,5-xylenol, but does not react with the hindered 6-t-butyl-2,4-xylenol. Steam distillation of the mixture then carried over this product(31).

Work carried out during recent years has led to selective ortho alkylation of phenols with open para positions. Based on selective ortho alkylation(32) Neuworth and his co-workers (33) have devised another route to 6-t-butyl-2,4-xylenol, starting with o-cresol (XI). t-Butylation under these conditions gives 6-t-butyl-o-cresol (XII) and a Mannich reaction on this with formaldehyde and dimethylamine yields 4-dimethylaminomethyl-6-t-butyl-o-cresol (XIII). This is then treated with hydrogen, to give 6-t-butyl-2,4-xylenol and dimethylamine as the products of the hydrogenolysis. The amine is then recycled to the Mannich reaction.

The work by Kolka, Ecke and their co-workers in this country (34,35) and by Stroh in Germany (36,37) has led to an economical synthesis of 2,6-di-t-butylphenol (XIV) which had been known for some time (38,39). This compound is presently marketed by Ethyl and it serves as starting material for a number of derivatives which are antioxidants in their own rights.

Besides the t-alkyl derivatives, specifically t-butyl derivatives, of tar acids, the α-methylbenzyl or styryl derivatives of the phenols are of great commercial importance as antioxidants. Specifically, styrenated phenol itself (XV) is probably the alkylated tar acid made in greatest amount for use as antioxidant. This material, however, is not a pure compound, and not even a mixture of positional isomers. Rather, it is the reaction product of the styrenation of phenol, and, therefore, could contain, along with mono-, di- and tri-styryl phenols, phenol substituted with low molecular weight polymers of styrene such as dimers and trimers. These would be the results of a preliminary polymerization of styrene followed by alkylation of phenol with the resultant oligomers. It is obvious that a complex mixture is possible. So-called "alkylated styrenated phenols" are also commercial products. While styrenation may be considered a special form of alkylation, the designation "alkylated styrenated," probably denotes the fact that these products contain both styryl and t-alkyl side chains on phenolic nuclei.

A second major group of phenolic antioxidants include those produced from phenols, especially sterically hindered ones such as t-alkylated phenols, via subsequent reactions. The most important subdivision of these is the group in which two or more phenolic nuclei have been linked together. The bridging of these nuclei may consist of a number of groups, predominantly alkylidene, such as methylidene, or thio groups. On the other hand, the phenolic nuclei may be directly linked to each other. While two routes present themselves for the preparation of these compounds, namely alkylation of the tar acids followed by coupling, and the reverse order, it is the first which is usually practiced to give industrially important antioxidants. Usually, only two phenolic groups are linked. The advantage of these higher molecular weight materials is low volatility, a desirable property both during the processing of polymers in which they find major use, and during the remainder of the life of the articles made from the polymers.

If pure p-cresol rather than a mixture of m- and p-cresol is alkylated with isobutylene, the monobutyl-p-cresol (III) can be readily separated by distillation from the other materials in the reaction mixture. These would be the unreacted p-cresol and BHT. The 2-t-butyl-p-cresol is then reacted with formaldehyde under acidic conditions to give 2,2'-methylenebis (4-methyl-6-t-butylphenol) (XVI) (40).

In a similar fashion, 2-t-butyl-4-ethylphenol can be prepared from 4-ethylphenol and then converted to its methylenebis derivative.

In the m-cresol series, the most important alkylidene derivative is 4,4'-butylidenebis (2-t-butyl-p-methylphenol) (XVII) obtained as the product from the condensation of 6-t-butyl-m-cresol (V) and butyraldehyde (41). However, since the only source of m-cresol is that admixed with its isomer, p-cresol, and since the two monobutyl derivatives of these could not be separated by distillation, the only

possible source of 6-t-butyl-m-cresol is the dibutyl-m-cresol (VI), which we obtained along with 2,6-di-t-butyl-p-cresol. Partial dealkylation of 4,6-di-t-butyl-m-cresol gives a mixture high in the desired 6-t-butyl-m-cresol along with m-cresol (IV) and unreacted starting material. The dealkylations in the presence of various catalysts take place under more severe temperature conditions than do the reverse alkylations. Two other bisphenols namely 4,4'-methylenebis (2,6-di-t-butylphenol) (XVIII) and 4,4'-methylene (6-t-butyl-o-cresol) (XIX) are now commercial products as a result of selective ortho alkylation. The latter is, of course, a derivative of o-cresol. The preparation of these bisphenols is carried out under basic conditions (42,43,44).

Trisphenols have also been made. However, only one (XX) derived from p-cresol, 2-t-butyl-p-cresol and formaldehyde, seems to be of commercial importance. The preparation of trisphenols is more complex than that of bisphenols. In the latter case only one compound is possible. In the preparation of trisphenols, a number of products are possible, and therefore, the reaction is carried out stepwise (45).

Almost all of the alkylidenebis compounds have thiobis counterparts, i.e. compounds in which the two phenol rings are coupled by a sulfur linkage. This coupling is accomplished by the reaction of the mononuclear phenolic compound with sulfur dichloride. Catalysts have been used in this reaction (46) but are not necessary. Of greatest importance is 4,4'-thiobis (6-t-butyl-m-cresol (XXI) (47). Others are the thiobis derivatives of 2-t-butyl-p-cresol (XXII) and 6-t-butyl-o-cresol (XXIII).

Several other phenolic antioxidants derived from tar acids have recently been introduced. All are the products of the reactions of ortho alkylated phenols. Starting with 2,6-di-t-butylphenol (XIV), oxidative coupling and reduction yields 4,4'-bis (2,6-di-t-butylphenol) (XXIV) (48). This is a biphenol in which the two phenolic rings are linked directly to each other. Two other antioxidants based on 2,6-di-t-butylphenol are the p-methoxymethyl and the p-dimethylaminomethyl derivatives. The former (XXV) is the product of the reaction of the phenol, formaldehyde and methanol (43,48,49,50). The amino (XXVI) compound results when the phenol, formaldehyde and dimethylamine are reacted in a Mannich reaction (48,51).

In summary, alkylation, especially t-butylation and styrenation of tar acids to give sterically hindered phenols is the most important chemical reaction for the preparation of antioxidants. Secondly, the joining together of two or more phenolic nuclei with each other via a phenol-aldehyde condensation, a phenol-sulfur dichloride condensation, or an oxidative coupling is of major importance. To a much lesser degree, the reaction of a phenol, an aldehyde and a third compound with a replaceably hydrogen leads to antioxidants.

When the major antioxidants are broken down according to the starting tar acids, it becomes apparent that phenol, o-cresol, m,p-cresol and 2,4-2,5-xylenol are the acids used to make the phenolic antioxidants. Phenol yields styrenated phenols, 2,6-di-t-butylphenol and its derivatives. o-Cresol yields the o-t-butyl derivative which is then converted to the methylenebis and the thiobis compound. p-Cresol is alkylated to 2-t-butyl-p-cresol as an intermediate for the manufacture of its methylenebis and thiobis derivatives, and to BHT. The monobutyl-p-cresol and the parent p-cresol are also reacted with formaldehyde to give 2,6-bis(2'hydroxy-3'-t-butyl-5'-methylbenzyl)-p-cresol, a trisphenol. m-Cresol is converted to its monobutyl derivative, 6-t-butyl-m-cresol, via the dibutyl derivative. The monobutyl cresol is then converted to its 4,4'-butylidenebis and its thiobis derivatives. Finally, a mixture of 2,4- and 2,5-xylenol is butylated and the 6-t-butyl-2,4-xylenol is isolated.

While this is a survey of tar acid-derived phenolic antioxidants, it must be remembered that there are other phenolic antioxidants, not derived from tar acids (just as there are non-phenolic antioxidants derived from tar acids). Even within the realm presented here, hundreds of structures have been prepared for antioxidant evaluation. Some of these are good antioxidants but have not been brought to commercialization for one reason or another.

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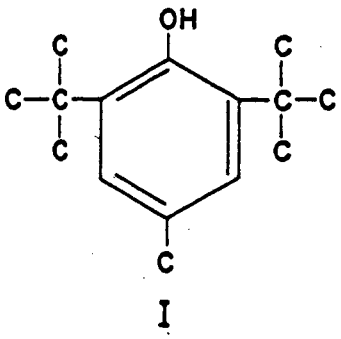

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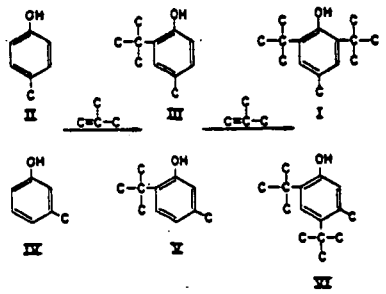

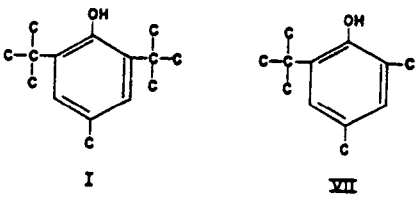

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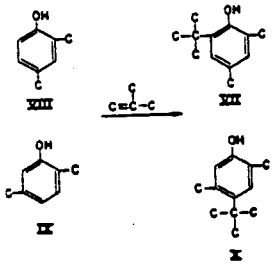

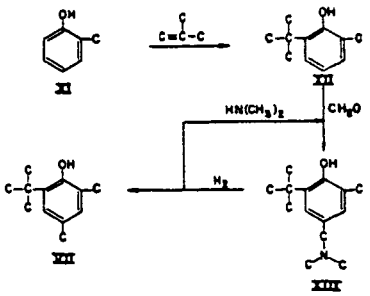

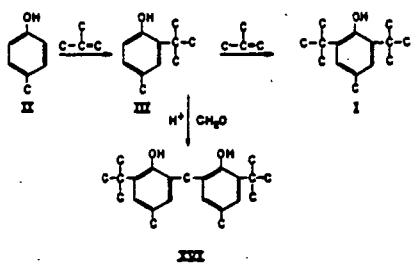

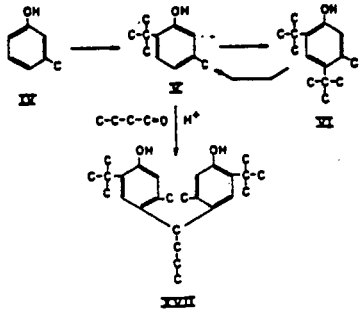

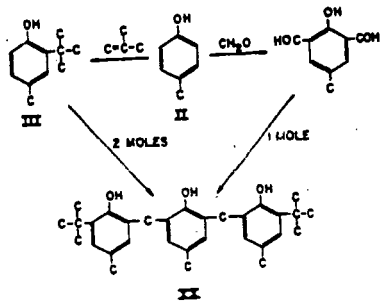

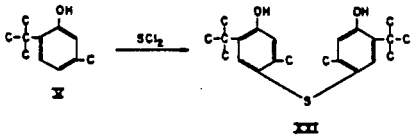

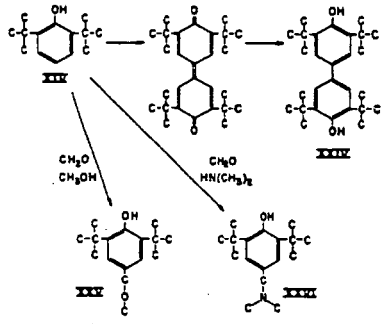

1) TAR ACID + OLEFIN $\xrightarrow{H^+}$ STERICALLY HINDERED PHENOLS.

2) a. ALKYLATED PHENOLS + ALDEHYDE $\xrightarrow{H^+}$ ALKYLIDENEBIS PHENOLS

b. ALKYLATED PHENOLS + SULFUR DICHLORIDE $\xrightarrow{H^+}$ THIOBIS PHENOLS

c. ALKYLATED PHENOLS $\xrightarrow[\text{COUPLING}]{\text{OXIDATIVE}}$ ALKYLATED BIPHENOLS

3) a. ALKYLATED PHENOLS + ALDEHYDE + AMINE $\longrightarrow$ AMINOMETHYLPHENOLS

b. ALKYLATED PHENOLS + ALDEHYOE + ALCOHOL $\longrightarrow$ ALKOXYMETHYLPHENOLS